Mössbauer and EPR Studies of Nitrogenase

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For the past 30 years we have studied in our laboratory the proteins of nitrogenase using Mössbauer and EPR spectroscopy. Although the MoFe protein seemed originally too complicated for working out the structures of (obviously) novel clusters, the protein was friendly in the sense that system could be manipulated into states were one cluster form was diamagnetic and the other paramagnetic, facilitating an in depth analysis of the Mössbauer spectra by tight correlation with EPR. Thanks to our cherished collaborators W. H. Orme-Johnson and B.G. Burgess we were able to explore the cluster structure of the MoFe protein and the Fe-protein in considerable detail. In 1978 we proposed, with a little trepidation, that the MoFe protein has 30 ± 2 Fe atoms, a prediction that proved to be correct, with a little bit of luck. While the oxidation states of all P-cluster irons, in the state P^N, were safely predicted to be all ferrous, the oxidation states of the cofactor irons were much more difficult to assess. The reason became abundantly clear when the first X-ray structure of the protein was reported in 1992. The discovery of the interstitial atom (N, C, or O) in the cofactor cage, in 2002, together with advances in density functional theory calculations suggested that the cofactor in the S = 3/2 state had (formally) four ferrous and three ferric ions. After a short historical excursion, we discuss some nitrogenase questions that can further be explored with Mössbauer spectroscopy.